



# Solid-Phase Extraction and Gas Chromatography/Mass Spectrometry Analysis of Selected Phenols

## Application

Environmental

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### Abstract

**Solid-phase extraction offers a simplified approach to the concentration of compounds present at trace levels in water. Polymeric resins, such as polystyrene-divinylbenzene, offer advantages over the commonly used octadecyl and similar silica-substrate solid-phase extraction adsorbents, especially for more polar compounds. Recently Agilent Technologies has expanded its offering of solid-phase extraction products to include a polystyrene-divinylbenzene solid-phase extraction material specifically for environmental applications, the AccuBond® ENV cartridge. Using the retention time locked gas chromatography/mass spectrometry analytical method previously described [1], this note makes an initial demonstration of the accuracy and precision that can be achieved for selected phenols at 10 ppb in water using this polystyrene-divinylbenzene solid-phase extraction material. The solid-phase extraction procedure is rapid, uses reduced drying times, and requires only two surrogates. The cartridge design has been optimized to provide increased recoveries for phenol, which**

**typically has low and irreproducible recoveries. Recoveries for phenol exceeded 70% and other phenols were greater than 90%. Precision was better than 5% and accuracy, as indicated by average absolute deviation as percent, was better than 8% for all phenols except 2-cyclohexyl-2,4-dinitrophenol. Sample delivery rate is high (20 to 25 mL/min) so a 1-liter sample can be extracted in less than an hour.**

### Introduction

Solid-phase extraction (SPE) has evolved to be a powerful tool for isolation and concentration of trace analytes in a variety of sample matrices. SPE has grown to replace liquid/liquid extraction due to the minimal use of solvent, the simplicity and flexibility of the approach, and the increased selectivity for analytes available. Beginning in and throughout the last decade, a large number of SPE applications were developed for compounds in matrices of environmental interest. The major focus of these applications was the collection and concentration of trace analytes from water. Most of the analytes were non-polar and strongly hydrophobic in nature such as polychlorinated biphenyls (PCBs), the organochlorine pesticides, polynuclear aromatic hydrocarbons (PAHs), for example, as these were relatively easy candidates for the technique and of widespread concern. More polar compounds like the phenols offer particular challenges.

SPE exploits the similarity in physicochemical properties of a class of analytes, their interaction with the SPE material, and their differences from the matrix. The phenols encompass a wide range in polarities and solubilities as shown in Table 1.



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The pKa values indicate that the dinitrophenol and the tetra- and penta-chloro phenols are fairly acidic and therefore are predominately dissociated in water at near-neutral pHs. Acid-base equilibrium considerations require that the water sample be acidified to at least 2 pH units below that of the lowest pKa value(s) to generate phenols primarily in their non-ionized form. Octanol-water partition constants ( $K_{ow}$ ) and water solubilities of the undissociated compounds range over a factor of more than several thousand. The high aqueous solubilities and low  $K_{ow}$  s of phenol and the monosubstituted phenols make these the most difficult phenols to capture and retain.

**Table 1. Physicochemical Properties of Some Phenols**

Compound	$\log_{10} K_{ow}$	pKa	Solubility <sub>(aq)</sub> g/L
Phenol	1.46	9.89	0.0884
4-chlorophenol	2.4	9.18	.027
4-methylphenol	1.96	10.26	.02
3-methylphenol	1.98	10	.022
4-nitrophenol	1.91	7.08	.013
2,4-dichlorophenol	3.2	7.68	.0045
2,4-dimethylphenol	2.35	10.6	.0088
2,4-dinitrophenol	1.67	4.09	.00034
2,4,6-trichlorophenol	3.69	7.42	.00043
2,3,4,6-tetrachlorophenol	4.45	5.38	.00018
Pentachlorophenol	5.05	4.92	0.000014

Polymeric resins were used early in the history of solid-phase extraction. These early materials needed extensive cleanup prior to use to avoid interferences obscuring analytes of interest. New generations of these polymers such as polystyrene-divinylbenzene (PS-DVB) have much lower backgrounds due to improvements in manufacturing processes. The use of PS-DVB polymers as an absorbent material has been demonstrated to provide improved recoveries for phenolic compounds as compared to the traditional and more commonly applied C18 material [2]. The details provided here ensure that analysts will observe less breakthrough of phenol, greatly improving overall recoveries.

The objective of this work was to develop a simple approach to SPE extraction and gas chromatography/mass spectrometry (GC/MS) analysis for selected phenols and perform a preliminary demonstration of accuracy and precision. A previous application note describes the retention-time locked GC/MS method in detail [1].

## Experimental

The phenols were obtained from Ultra Scientific (North Kingstown, RI) and AccuStandard (New Haven, CT) as mixtures. Dilutions were made in acetone and in dichloromethane (Burdick and Jackson Grade, VWR Scientific, San Francisco, CA) for surrogates or spiking and standards, respectively. Sodium sulfate (analytical grade, VWR Scientific, San Francisco, CA) was kilned at 500 °C and stored in a desiccator.

Empty 6-mL cartridges and frits were obtained from Agilent Technologies Inc. (Wilmington, DE) for use as drying cartridges. AccuBond<sup>II</sup> ENV PS-DVB cartridges containing 1000 milligrams of PS-DVB sorbent in a 6-mL cartridge were obtained from Agilent Technologies Inc. (Wilmington, DE). A summary of the equipment and consumables is given in Table 2.

**Table 2. Equipment and Consumables Summary**

Description	Part Number
Silanized amber vials	5183-4496
Vial crimp caps	5181-1210
AccuBond <sup>II</sup> ENV PS-DVB polymeric resin as 1000 mg / 6-mL cartridge, box of 30	188-3060
Empty SPE Cartridges Reservoirs, 6 mL, box of 50	700-4006
Frits for 6 mL cartridges reservoirs, 100/pk	700-4031
Stopcock valves, 10/pk	5185-5758
SPE Manifold, 10-port	5185-5754
SPE Manifold, 20-port	5185-7565

## Spike and Recovery Experiments

For the initial demonstration of the accuracy and precision of the approach, 1.0 L of deionized RO water was spiked with 21 phenols at 10 pbb each. Deuterated phenol, 2,4-dibromophenol, and 2,4,6-tribromophenol were added at 10 ppb as recovery surrogates. Three “calibrators” were also made at that time by adding the spike and surrogates to a silanized vial containing some dichloromethane (DCM) as a keeper. The solution was mixed and the pH lowered to  $\leq 2$  with 5N HCl.

The PS-DVB SPE cartridge was conditioned by sequentially rinsing with 9 to 12 mL of DCM, 9 to 12 mL of methanol, and 9 to 12 mL of 0.05N HCl. At no time after the initial addition of DCM was the column allowed to run dry.

The 1-L water sample was then pulled through the SPE cartridge at a flow between 20 and 25 mL/min such that the sample was processed in less than 1 hour. The SPE cartridge was dried briefly by drawing clean laboratory air through the cartridge for about 2 minutes while tapping the cartridge body to dislodge bound water. The SPE cartridge was then eluted with 9 mL of DCM. The DCM eluant was dried using a cartridge filled with anhydrous sodium sulfate.

The dried DCM eluant was evaporated under dry, filtered nitrogen and transferred to a silanized amber vial. At this point, the volumes of the sample and the three calibrators were brought to approximately 0.9 mL and 100  $\mu$ L of a solution containing 2,5-dibromotoluene and 2,2',5,5'-tetrabromobiphenyl at 0.05  $\mu$ g/ $\mu$ L in DCM was added as internal (injection) standards. A solvent blank, the three calibrators and the sample were then

analyzed using an Agilent 6890 Plus GC and 5973N MSD according to operating parameters given in a previous note [1].

## Results and Discussion

Corrected and uncorrected results of inter-day replicates for selected phenols are shown in Table 3. Phenol values were corrected to the deuterated phenol while all other compounds were corrected to 2,4-dibromophenol recoveries. With the exception of the 2-cyclohexyl-2,4-dinitrophenol, all RSD values and deviations are under 5% and 8%, respectively. The average RSD and absolute deviation for all the compounds are 4% and 6%, respectively. These indicate very good reproducibility and accuracy. An anomalously high value in the third trial seems to have inflated the deviation for 2-cyclohexyl-2,4-dinitrophenol.

**Table 3. Spike and recovery results for accuracy and precision at 10 ppb using the AccuBond<sup>®</sup> ENV SPE cartridge. The average deviation is calculated as the relative average of the absolute deviations from 10 ppb and expressed as percentages. RSD represents the relative standard deviations.**

Trial Number: Compound	Trial #1		Trial #2		Trial #3		RSD %	Average Deviation
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected		
Phenol	7.8	10.7	7.2	10.3	7.7	11.0	3%	7%
2-chlorophenol	9.8	9.3	9	8.9	10.3	9.3	3%	8%
2-methylphenol	9.9	9.4	9.1	9.0	10.5	9.5	3%	7%
3- & 4-methylphenol	9.8	9.3	9.2	9.1	10.4	9.4	2%	7%
2,4-dimethylphenol	9.9	9.4	9.4	9.3	10.5	9.5	1%	6%
2-nitrophenol	10.0	9.5	9.1	9.0	10.7	9.6	4%	6%
2,4-dichlorophenol	9.9	9.4	9.1	9.0	10.5	9.5	3%	7%
2,6-dichlorophenol	9.7	9.2	9.1	9.0	10.4	9.4	2%	8%
4-chloro-3-methylphenol	10.1	9.6	9.3	9.2	10.7	9.6	3%	5%
2,4-dibromophenol	10.5		10.1		11.1			
2,4,6-trichlorophenol	9.7	9.2	9.1	9.0	10.6	9.5	3%	7%
2,4,5-trichlorophenol	9.8	9.3	9.1	9.0	10.4	9.4	2%	8%
4-nitrophenol	10.0	9.5	9.8	9.7	11.5	10.4	4%	4%
2,3,4,5-tetrachlorophenol	9.7	9.2	9.3	9.2	10.7	9.6	3%	6%
2,3,5,6-tetrachlorophenol	9.9	9.4	9.1	9.0	10.4	9.4	2%	7%
2,3,4,6-tetrachlorophenol	9.8	9.3	9.3	9.2	10.6	9.5	2%	6%
2,4-dinitrophenol	10.6	10.1	9.8	9.7	11.9	10.7	5%	4%
2,4,6-tribromophenol	9.7	9.2	9.6	9.5	10.7	9.6	2%	5%
2-methyl-4,6-dinitrophenol	10.1	9.6	9.5	9.4	11.4	10.3	5%	4%
Pentachlorophenol	9.8	9.3	9.5	9.4	11.1	10.0	4%	4%
Dinoseb	10.2	9.7	9.4	9.3	11.5	10.4	5%	4%
2-cyclohexyl-4,6-dinitrophenol	11.2	10.7	10.6	10.5	14.4	13.0	12%	14%
2,2',5,5'-tetrabromobiphenyl	10.5	10.0	10.5	10.4	12.3	11.1	5%	5%

Typically, a 1-gram sorbent cartridge is considered an excessive use of material. However, work with 500-mg cartridges showed recoveries for phenol near and below 50%. Tandem cartridges revealed substantial phenol on the second cartridge. Increasing the polymer mass to 1 gram reduced breakthrough and consequently increased phenol recoveries. The methylphenols also demonstrated this behavior to a lesser degree and supported the change in sorbent bed mass.

Using a single surrogate to correct all the substituted phenols seems a tremendous simplification since the behavior and chemistries of the phenols differ widely. It is likely that this will become apparent at lower concentrations and most likely for the nitrophenols. Data does imply that the tetrabromobiphenyl (included in Table 3) may allow a better correction of the injection volume for the late eluters.

## Conclusions

These preliminary results show that phenols can be extracted from aqueous samples accurately and precisely using AccuBond<sup>II</sup> ENV PS-DVB polymeric resin. Coupled with a gas chromatographic analysis and retention time locking GC/MS [1], extraction, identification and quantitation of phenolic compounds can be done confidently, accurately and reproducibly. This method is a modification of U.S. EPA Method 528 [3]. The procedure here for the extraction of phenols from drinking water by polymeric SPE results in improved recoveries and greatly reduced drying times (2 minutes compared to 20 minutes), which increases sample throughput. The next steps in developing a full method

would be an exploration of detection limits which will require extraction of replicates at lower concentrations. It is expected that the behavior of the more "active" compounds may suggest an expanded suite of surrogates.

## References

1. Reese, A. and H. Prest, *Retention Time Locked GC/MS Analysis of Phenols*, 5988-3934EN, [www.agilent.com/chem](http://www.agilent.com/chem)
2. Rodriguez, Llompart and Cela, *Solid-phase extraction of phenols*, Journal of Chromatography A, 885 (2000) 291-304.
3. Munch, EPA Method 528, *Determination of Phenols in Drinking Water by Solid-Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)* Revision 1 (April 2000).

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